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Dissociation constants and thermodynamic properties of alkanolamines

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Abstract

The dissociation constants of protonated 2-amino-2-ethyl-1,3-propanediol (AEPD), 2-amino-2-methyl-1-propanol (AMP), diethylmonoethanolamine (DEMEA), diisopropanolamine (DIPA), dimethylmonoethanolamine (DMMEA), monoethanolamine (MEA), 1-amino-2-propanol (MIPA), and methylmonoethanolamine (MMEA) have been determined by electromotive force measurements from (293 to 353) K. The experimental results and derived values of the standard state thermodynamic properties are reported.

Keywords: dissociation; ionization; protonation; alkanolamine; enthalpy, gibbs free energy, basic strength

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1. Introduction

Aqueous solutions of (alkanol)amines are frequently used for the removal of acid gases, such as CO_2 and H_2S, from a variety of gas streams. The dissociation constant is one of the important parameters in the selection of an (alkanol)amine solution for acid gas removal or in the interpretation of the kinetic mechanism of the (alkanol)amine with CO_2. Temperature dependent dissociation constants describe the change of the basic strength of an absorbent as the temperature is changed, alike the temperature cycle in a traditional absorber-desorber cycle. [1]

The dissociation constants of protonated 2-amino-2-ethyl-1,3-propanediol (AEPD), 2-amino-2-methyl-1-propanol (AMP), diethylmonoethanolamine (DEMEA), diisopropanolamine (DIPA), dimethylmonoethanolamine (DMMEA), monoethanolamine (MEA), 1-amino-2-propanol (MIPA), and methylmonoethanolamine (MMEA) have been determined by electromotive force measurements from (293 to 353) K.

2. Theory and experimental procedure

A protonated alkanolamine dissociates according to:

$$BH^+ + H_2O \rightleftarrows B + H_3O^+ \tag{1}$$

where B is an alkanolamine. The equilibrium constant can be determined by electromotive force (EMF) measurements using a combined glass pH electrode. [2] A two-cell system was used:

$$Ag(s), AgCl(s) \mid 3\ M\ KCl(aq) \mid\mid HCl(aq, \bar{m}_{HCl}) \mid\mid Glass\ Electrode \tag{I}$$

and

$$Ag(s), AgCl(s) \mid 3\ M\ KCl(aq) \mid\mid HCl(aq, \bar{m}_{HCl}), B(aq, \bar{m}_B) \mid\mid Glass\ Electrode \tag{II}$$

The activity of a pure solid was set to unity and the Nernst equation for cell I is:

$$E_I = E^0(T_I) - \frac{RT_I}{F} \ln\left(a_{H_3O^+} a_{Cl^-}\right)_I \tag{2}$$

and for cell II:

$$E_{II} = E^0(T_{II}) - \frac{RT_{II}}{F} \ln\left(a_{H_3O^+} a_{Cl^-}\right)_{II} \tag{3}$$

As both cells were kept at the same temperature, the standard potential of the combined glass pH electrode, $E^0(T)$, was the same during both measurements:

$$T_{II} \ln\left(a_{H_3O^+} a_{Cl^-}\right)_{II} = \frac{F(E_I - E_{II})}{R} + T_I \ln\left(a_{H_3O^+} a_{Cl^-}\right)_I \tag{4}$$

HCl was completely dissociated in cell I; thus the dissociation of water in cell I was neglected. The mole balances of the alkanolamine, HCl, and water in cell II are:

$$\bar{n}_B = n_B + n_{BH^+} \tag{5}$$

$$\bar{n}_{HCl} = n_{Cl^-} \tag{6}$$

$$\bar{n}_{H_2O} = n_{H_2O} + n_{H_3O^+} + n_{OH^-} \tag{7}$$

Electroneutrality results in:

$$n_{BH^+} + n_{H_3O^+} = n_{Cl^-} + n_{OH^-} \tag{8}$$

The chemical equilibrium for reactions present are:

$$K_W(T) = \frac{a_{H_3O^+} a_{OH^-}}{a_{H_2O}^2} \tag{9}$$

$$K(T) = \frac{a_B a_{H_3O^+}}{a_{BH^+} a_{H_2O}} \tag{10}$$

For a given temperature and composition, the electromotive forces, E_I and E_{II}, and the temperatures, T_I and T_{II}, were measured. The activities of HCl and KCl were estimated using the excess energy model of Pitzer. Activities of the compounds present in cell II were approximated using the modified Debye-Huckel term in Pitzer's equation, i.e. neglecting the binary and ternary interaction parameters. The activity coefficient for the unprotonated alkanolamine was set to unity for all molalities and temperatures. The activity of water followed from the Gibbs-Duhem equation. A further detailed and comprehensive experimental procedure can be found elsewhere. [3] [4] Equation (4) to (10) were solved iteratively to yield the "true" number of moles of the species present in cell II, as well as a preliminary value of the dissociation constant. This dissociation constant was calculated out of a set of equations in which for cell II the activity coefficients were not exactly known. The experiments were carried out at different overall molalities of the alkanolamine, and the dissociation constant of the alkanolamine was determined in a two-step linear extrapolation procedure:

$$\lim_{\substack{\bar{m}_{HCl,II}=const \\ \bar{m}_B \to 0}} \left[K_{exptl}(T, \bar{m}_B, \bar{m}_{HCl,II})\right] = K_{exptl}(T, \bar{m}_{HCl,II}) \tag{11}$$

$$\lim_{\bar{m}_{HCl,II} \to 0} \left[K_{exptl}(T, \bar{m}_{HCl,II})\right] = K(T) \tag{12}$$

Since $\bar{m}_{HCl,II}$ was less than approximately 0.01 mol/kg solvent, the second extrapolation was not necessary.

3. Thermodynamic relations

To the experimentally determined dissociation constants, the well-known thermodynamic relations were applied:

$$\Delta_r G_m = -RT \ln K \tag{13}$$

$$\Delta_r H_m = -R \frac{d \ln K}{d(1/T)} \tag{14}$$

and the change of the standard state properties ($T = T^0 = 298.15$ K) for the dissociation of an alkanolamine in water were calculated. The further thermodynamic relations such as the molar change of the reaction entropy and the change in heat capacity can be calculated by the reader.

4. Experimental

A pH voltmeter (Metrohm 780) and a combined pH electrode (Metrohm 6.0258.010) were used for the EMF measurements. The electrode was equipped with a built-in PT1000 temperature sensor and an inner 3 M KCl solution (Metrohm 6.2308.020). Before each measurement, the electrode was carefully rinsed with distilled

water and dried with paper tissue. Cell I and II were completely filled with the electrolyte solutions, placed in a water bath for temperature control, and sealed between each measurement. The experiments were performed inside a glove box to prevent CO_2 absorption from air. During each measurement the electromotive force, E, and the temperature, T, were recorded.

5. Results and discussion

Experimental results at averaged temperatures for the dissociation constants of protonated AEPD, AMP, DEMEA, DIPA, DMMEA, MEA, MIPA, and MMEA are given in Table 1. The changes of the molar Gibbs free energy and the molar reaction enthalpy are given in Table 2 together with the calculated pK_a values at 298.15 K for the convenience of the reader.

Table 1: Dissociation constants of protonated amines

Run	T / K	ln(K)	Run	T / K	ln(K)	Run	T / K	ln(K)
	AEPD			AMP			DEMEA	
1	293.12	-20.63 ± 0.04	1	293.16	-22.69 ± 0.04	1	293.17	-22.69 ± 0.04
2	293.05	-20.63 ± 0.04	2	293.12	-22.66 ± 0.04	2	293.15	-22.73 ± 0.04
3	293.06	-20.63 ± 0.04	3	293.19	-22.61 ± 0.04	3	293.13	-22.60 ± 0.04
4	298.26	-20.31 ± 0.04	4	298.06	-22.27 ± 0.04	4	298.16	-22.51 ± 0.04
5	298.33	-20.29 ± 0.04	5	298.14	-22.33 ± 0.04	5	298.13	-22.47 ± 0.04
6	298.29	-20.26 ± 0.04	6	298.09	-22.23 ± 0.04	6	298.07	-22.41 ± 0.04
7	303.16	-19.99 ± 0.04	7	303.15	-21.96 ± 0.04	7	303.35	-22.22 ± 0.04
8	303.28	-19.97 ± 0.04	8	303.08	-21.94 ± 0.04	8	303.30	-22.22 ± 0.04
9	303.30	-19.96 ± 0.04	9	303.16	-21.89 ± 0.04	9	303.29	-22.17 ± 0.04
10	312.89	-19.40 ± 0.04	10	313.18	-21.27 ± 0.04	10	313.36	-21.71 ± 0.04
11	312.96	-19.39 ± 0.04	11	313.06	-21.30 ± 0.04	11	313.32	-21.73 ± 0.04
12	312.95	-19.40 ± 0.04	12	313.15	-21.25 ± 0.04	12	313.16	-21.71 ± 0.04
13	322.96	-18.81 ± 0.04	13	323.26	-20.65 ± 0.04	13	323.10	-21.25 ± 0.04
14	323.04	-18.81 ± 0.04	14	323.43	-20.63 ± 0.04	14	323.01	-21.23 ± 0.04
15	322.98	-18.81 ± 0.04	15	323.28	-20.62 ± 0.04	15	322.96	-21.23 ± 0.04
16	333.09	-18.26 ± 0.04	16	333.16	-20.04 ± 0.04	16	333.05	-20.75 ± 0.04
17	333.23	-18.26 ± 0.04	17	333.15	-20.06 ± 0.04	17	333.01	-20.77 ± 0.04
18	333.05	-18.26 ± 0.04	18	333.10	-19.99 ± 0.04	18	332.92	-20.78 ± 0.04
19	343.11	-17.73 ± 0.04	19	343.04	-19.46 ± 0.04	19	342.93	-20.27 ± 0.04
20	342.97	-17.74 ± 0.04	20	343.01	-19.52 ± 0.04	20	342.86	-20.30 ± 0.04
21	342.93	-17.76 ± 0.04	21	342.90	-19.43 ± 0.04	21	342.75	-20.30 ± 0.04
22	353.11	-17.26 ± 0.04	22	353.22	-18.93 ± 0.04	22	353.11	-19.84 ± 0.04
23	353.21	-17.26 ± 0.04	23	353.14	-18.95 ± 0.04	23	353.03	-19.85 ± 0.03
24	353.12	-17.27 ± 0.04	24	353.03	-18.87 ± 0.04	24	353.11	-19.84 ± 0.03
	DIPA			DMMEA			MEA	
1	293.05	-20.60 ± 0.04	1	293.27	-21.48 ± 0.04	1	293.11	-22.07 ± 0.04
2	293.07	-20.66 ± 0.04	2	293.24	-21.46 ± 0.04	2	293.11	-22.09 ± 0.04
3	293.19	-20.62 ± 0.04	3	293.26	-21.45 ± 0.04	3	293.09	-22.08 ± 0.04
4	298.11	-20.32 ± 0.04	4	298.18	-21.23 ± 0.04	4	298.34	-21.71 ± 0.04
5	298.02	-20.37 ± 0.04	5	298.17	-21.22 ± 0.04	5	298.24	-21.73 ± 0.04

6	298.09	-20.42 ± 0.04	6	298.29	-21.21 ± 0.04	6	298.05	-21.76 ± 0.04
7	303.26	-20.08 ± 0.04	7	298.29	-21.01 ± 0.04	7	303.11	-21.44 ± 0.04
8	303.34	-20.08 ± 0.04	8	303.28	-20.98 ± 0.04	8	303.04	-21.42 ± 0.04
9	303.36	-20.09 ± 0.04	9	303.38	-20.98 ± 0.04	9	302.98	-21.44 ± 0.04
10	313.24	-19.59 ± 0.04	10	313.29	-20.55 ± 0.04	10	313.07	-20.80 ± 0.04
11	313.25	-19.59 ± 0.04	11	313.36	-20.56 ± 0.04	11	313.17	-20.80 ± 0.04
12	313.26	-19.60 ± 0.04	12	313.41	-20.53 ± 0.04	12	313.22	-20.80 ± 0.04
13	323.14	-19.07 ± 0.04	13	323.36	-20.10 ± 0.04	13	323.20	-20.20 ± 0.04
14	323.18	-19.07 ± 0.04	14	323.45	-20.10 ± 0.04	14	323.34	-20.20 ± 0.04
15	323.16	-19.10 ± 0.04	15	323.44	-20.08 ± 0.04	15	323.32	-20.20 ± 0.04
16	333.12	-18.61 ± 0.04	16	333.46	-19.65 ± 0.04	16	333.24	-19.62 ± 0.04
17	333.17	-18.61 ± 0.04	17	333.53	-19.65 ± 0.04	17	333.28	-19.64 ± 0.04
18	333.16	-18.62 ± 0.04	18	333.48	-19.66 ± 0.04	18	333.20	-19.66 ± 0.04
19	343.10	-18.12 ± 0.04	19	343.20	-19.21 ± 0.04	19	343.14	-19.11 ± 0.04
20	343.09	-18.14 ± 0.04	20	343.16	-19.24 ± 0.04	20	343.17	-19.13 ± 0.04
21	343.00	-18.16 ± 0.03	21	343.14	-19.25 ± 0.04	21	343.12	-19.13 ± 0.04
22	353.11	-17.72 ± 0.03	22	353.14	-18.86 ± 0.03	22	353.14	-18.60 ± 0.03
23	353.06	-17.69 ± 0.04	23	353.19	-18.84 ± 0.03	23	353.26	-18.61 ± 0.03
24	352.92	-17.71 ± 0.03	24	353.22	-18.83 ± 0.03	24	353.14	-18.64 ± 0.03

	MIPA			MMEA	
1	293.26	-22.10 ± 0.04	1	293.14	-22.97 ± 0.04
2	293.51	-22.07 ± 0.04	2	293.07	-22.97 ± 0.04
3	293.26	-22.09 ± 0.04	3	293.16	-22.98 ± 0.04
4	298.36	-21.75 ± 0.04	4	298.13	-22.69 ± 0.04
5	298.38	-21.75 ± 0.04	5	298.15	-22.65 ± 0.04
6	298.47	-21.74 ± 0.04	6	298.20	-22.67 ± 0.04
7	303.25	-21.42 ± 0.04	7	303.25	-22.38 ± 0.04
8	303.32	-21.40 ± 0.04	8	303.14	-22.37 ± 0.04
9	303.15	-21.44 ± 0.04	9	303.14	-22.39 ± 0.04
10	313.06	-20.82 ± 0.04	10	313.26	-21.80 ± 0.04
11	313.08	-20.82 ± 0.04	11	313.21	-21.78 ± 0.04
12	313.11	-20.82 ± 0.04	12	313.11	-21.80 ± 0.04
13	323.27	-20.20 ± 0.04	13	323.51	-21.25 ± 0.04
14	323.32	-20.20 ± 0.04	14	323.24	-21.22 ± 0.04
15	323.24	-20.21 ± 0.04	15	323.12	-21.23 ± 0.04
16	333.35	-19.63 ± 0.04	16	333.15	-20.72 ± 0.04
17	333.42	-19.62 ± 0.04	17	333.14	-20.70 ± 0.04
18	333.41	-19.64 ± 0.04	18	333.11	-20.71 ± 0.04
19	343.15	-19.09 ± 0.03	19	343.17	-20.20 ± 0.04
20	343.26	-19.12 ± 0.04	20	343.21	-20.18 ± 0.04
21	343.15	-19.11 ± 0.04	21	343.13	-20.21 ± 0.04
22	353.19	-18.56 ± 0.03	22	353.16	-19.70 ± 0.04
23	353.24	-18.58 ± 0.04	23	353.20	-19.70 ± 0.03
24	353.12	-18.59 ± 0.03	24	353.14	-19.71 ± 0.04

Table 2: Values of the standard state thermodynamic properties

	$\Delta_r G_m$ / kJ mol^{-1}	pK_a	$\Delta_r H_m$ / kJ mol^{-1}
AEPD	50.32	8.82	47.5
AMP	55.24	9.68	52.2
DEMEA	55.64	9.75	36.2
DIPA	50.47	8.84	39.2
DMMEA	52.63	9.22	34.4
MEA	53.90	9.44	48.6
MIPA	53.94	9.45	48.8
MMEA	56.20	9.85	44.4

In an absorption-desorption cycle, the temperature is usually varied from about (313 to 393) K depending on the operating condition. [1] The change in the molar reaction enthalpy in Table 2 specifies the shifting basic strength of the alkanolamine within a specific temperature interval; i.e. the change of the basic strength of the absorbent between an absorber and a desorber due to the temperature cycle. As seen from Table 2; AMP has the highest molar change in reaction enthalpy, whereas the tertiary alkanolamine DMMEA has the lowest.

6. Conclusion

The dissociation constants of protonated AEPD, AMP, DEMEA, DIPA, DMMEA, MEA, MIPA, and MMEA have been determined by electromotive force measurements from (293 to 353) K. The dissociation constants and the thermodynamic properties presented gives information about these alkanolamines as possible absorbents for acid gas removal.

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